Adsorption of Polar Molecules onto Electrodes Driven by the Combined Effects of Dielectric Inhomogeneity and Electrostatic Correlation

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Water dissolved in ionic liquids draws particular attention in electrochemistry, as represented in the case where water molecules cannot be removed entirely from ionic liquids. A recent atomistic molecular dynamics simulation suggested that water molecules in ionic liquids are significantly adsorbed onto electrodes, but an understanding of this mechanism is limited. To clarify the simulation data, we highlight the effects of the spatially varying dielectric response of the water and ionic liquid near charged plates by developing a coarse-grained mean-field theory that simultaneously accounts for both the permanent and induced dipole moments of the species, and the strong electrostatic correlation. We then demonstrate that polar molecules such as water may be enriched in the vicinity of electrodes primarily by the effects of the dielectric contrast between the species, and even markedly bound onto the charged surfaces when the electrostatic correlations are combined. A higher-dielectric component preferentially solvates electrodes, but this effect competes with that of the charge screening. Furthermore, we show that the energy efficiency may be improved through tuning the dielectric contrast within a certain range of the applied voltage. Our results predict that the linear-dielectric theory is inadequate to account for the correlation between the capacitance and dielectric contrast, which may be fitted by exponential functions. Our results compare favorably with previous molecular dynamics simulations.